Polymerization of *N*-benzylpropargylamine in the presence of ionic rhodium(I) complexes. A new functionalized polyacetylene: investigation of its conducting properties

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The polymerization reaction of *N*-benzylpropargylamine in the presence of rhodium complexes [Rh(L–L)chel)X (L–L = cycloocta-1,5-diene, 2,5-norbornadiene; chel = 2,2′-bipyridine, 2,2′-bipyrazine, 2,2′-dipyridylamine; $X = PF_6^-$, ClO_4^-, $B(Ph)_4^-$) and methanolic NaOH as co-catalyst gave polymers with molecular weights between about 1000 and 4000. Similar results were obtained with the platinum bisacetylide complex $[Pt(C{\equiv}CCH_2NHCH_2Ph)_2(PPh_3)_2]$, which was, however, less active than the rhodium compounds. Infra-red and ^1H nuclear magnetic resonance spectra of the different products were studied. The polymers so formed are insulators, but their conductivity increases on doping by over several orders of magnitude.

(Keywords: *N*-benzylpropargylamine polymers; doping; conductivity measurements)

INTRODUCTION

In the last few years great attention has been focused on polyacetylene, a polymer whose conductivity can be varied over several orders of magnitude by doping. However, this polymer is very sensitive to moisture and oxygen and its practical applications are limited[1,2].

We have now prepared a new polymer, $(-CH{=}CR-)_n$ ($R = -CH_2NHCH_2Ph$), stable in air, which shows conducting properties similar to those of polyacetylene. It was prepared by polymerization of *N*-benzylpropargylamine in the presence of several anionic rhodium(I) complexes or of *trans*-$[Pt(C{\equiv}CCH_2NHCH_2Ph)_2(PPh_3)_2]$. Results are given below.

EXPERIMENTAL

Reagents

The catalysts used for the polymerization were rhodium(I) complexes of the general formula [Rh(L–L)chel)X (L–L = *cis,cis*-cycloocta-1,5-diene (cod), 2,5-norbornadiene viz. bicyclo[2,2,1]hepta-2,5-diene (nbd); chel = 2,2′-bipyridine (bipy), 2,2′-bipyrazine (bpz), 2,2′-dipyridylamine viz. *N*-2-pyridinyl-2-pyridinamine (dipyam); $X = PF_6^-$, ClO_4^-, $B(Ph)_4^-$). Among them the bipy[3] and bpz[4] derivatives are known in the literature. The dipyam complexes were prepared by similar methods. Both compounds, i.e. $[Rh(cod)dipyam]PF_6$ and $[Rh(nbd)dipyam]PF_6$, are very soluble in acetone, dimethyl sulphoxide and acetonitrile and dissolve well also in methylene chloride; their solubility is poor in methanol and dichloroethane and negligible in chloroform, carbon tetrachloride, carbon disulphide, ether and water.

$[Rh(cod)dipyam]PF_6$–$[Rh(cod)Cl]_2$ (Strem. Chem. Inc.) (0.5 g, 1.01 mmol) was suspended in deaerated aqueous acetone (20 ml, 1:1), and solid dipyam (Fluka) (0.35 g, 2.04 mmol) was added under stirring. The starting complex dissolved slowly, giving a yellow-orange solution. After 1 h this was filtered and treated with a concentrated aqueous solution of NH_4PF_6 (0.5 g, 3.07 mmol). After 10 min yellow crystals began to precipitate. They were collected, washed with water and ether, and dried *in vacuo*. Yield: 0.65 g, 60.8 %. Analysis—calc. for $[RhC_{18}H_{21}N_3]PF_6$: Rh 19.52, C 41.0, H 4.01, N 7.97; found: Rh 19.4, C 40.7, H 4.20, N 7.95. I.r.* (KBr) (cm^{-1}): 3377 m (NH stretch); 1625 ms (Py I); 1582 m (Py II); 1524 mw; 1466 vs,br (Py III); 1432 sh, 1430 mw (Py IV?); 1414 w; 1350 mw; 1234 mw; sh 1163 m; 880 sh, 841 vs, br (PF_6); 777, 772 m, 741 mw, 693 w, br; 558 ms (PF_6); 530 mw.

$[Rh(nbd)dipyam]PF_6$ preparation was as above, with nbd as ligand. Analysis—calc. for $[RhC_{17}H_{17}N_3]PF_6$: Rh 20.13, C 39.94, H 3.35, N 8.22; found: Rh 20.0, C 39.4, H 3.44, N 8.06. I.r.* (KBr) (cm^{-1}): 3391 m (NH stretch); 1641 s (Py I); 1587 m (Py II); 1532 mw; 1484 s, br (Py III); 1432 (Py IV?); 1421, 1414 triplet, mw; 1232 m; 1170 m; 880 sh, 870, 842 vs, br (PF_6); 830 sh; 762 m; 560 (PF_6).

The complex $[Pt(C{\equiv}CCH_2NHCH_2Ph)_2(PPh_3)_2]$ was prepared as previously reported[6].

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* As found for dipyam protonated complexes of other metals[5], the first three vibrational bands of pyridine rings show appreciable shifts to higher energies in comparison to those of the free ligand. The presence of NH stretching vibration indicates that in these complexes only the ring nitrogens are involved in bonding to the metal ion

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A 0.2 M solution of NaOH in methanol was used as co-catalyst. *N*-Benzylpropargylamine (BPA) (Aldrich) was distilled under vacuum before use. All the solvents (C. Erba) were reagent grade and were used without further purification. If not otherwise specified, the reactions were carried out in a nitrogen atmosphere.

Polymerization procedure

In a typical experiment 40 mg of a complex and 3 ml of *N*-benzylproparglyamine were introduced into a 50 ml reaction vessel under nitrogen, then 0.1 ml of the NaOH solution (0.02 mmol) was added and the mixture was refluxed for 8 h.

The mixture turned brown. At the end of the reaction the viscous mass was treated with CCl_4. In most cases a homogeneous solution was obtained, but in the presence of [Rh(cod)bpz]PF_6, [Rh(cod)bipy]ClO_4 and [Rh(cod)bipy]BPh_4 complexes a residual fraction insoluble in CCl_4 was obtained and was separated by filtration. By treating the CCl_4 solution with petroleum ether the polymer (PBPA) separated as a brown powder, which was dried under vacuum. PBPA is soluble in halogenated organic solvents, ethers and benzene and insoluble in alcohols. It is also soluble in water acidified with H_2SO_4 and can be reprecipitated by addition of NaOH.

Doping procedure

First 200 mg of PBPA was dissolved in 20 ml of tetrahydrofuran (THF) (solution A). A solution of I_2 in THF (750 mg of I_2 in 25 ml of THF) was prepared (solution B). Then 5 ml (or 10 or 20 ml) of solution B were added to solution A and the mixture was stored at room temperature for about 12 h. The solvent was eliminated under vacuum. At low I_2 concentrations a brittle film of the doped polymer covered the walls of the vessel. The vitreous residue was powdered in a mortar and pellets were prepared in an i.r. pellet press at a pressure of about 8 tons. The pellets were used for conductivity measurements. At the highest dopant concentrations, a gummy mass was obtained even when the dopant polymer was stored under dynamic vacuum for 24–48 h. This gummy material was used directly to cover the electrodes for conductivity measurements.

Sometimes pellets with a low amount of I_2 were redissolved in THF and a new portion of the I_2 solution was added. The above procedure was repeated several times to increase the dopant concentration in a given sample.

The doped PBPA turns a dark brown-black colour; it is soluble in acetone and THF and insoluble in chlorinated solvents.

Apparatus

I.r. spectra were run on Perkin–Elmer model 580 B, Perkin–Elmer model 577 and Perkin–Elmer 983 G spectrophotometers. N.m.r. spectra were recorded on a EM Varian 60 spectrometer.

The d.c. conductivity measurements were carried out using a Keithley 616 electrometer. The cell used is shown in *Figure 1*. In some cases two gold discs were inserted between the brass electrodes and the pellet. No significant variations in the conductivity values were observed with the gold electrodes.

Molecular weights of PBPA were determined in $CHCl_3$ by a Knauer model 1100 osmometer at 37°C.

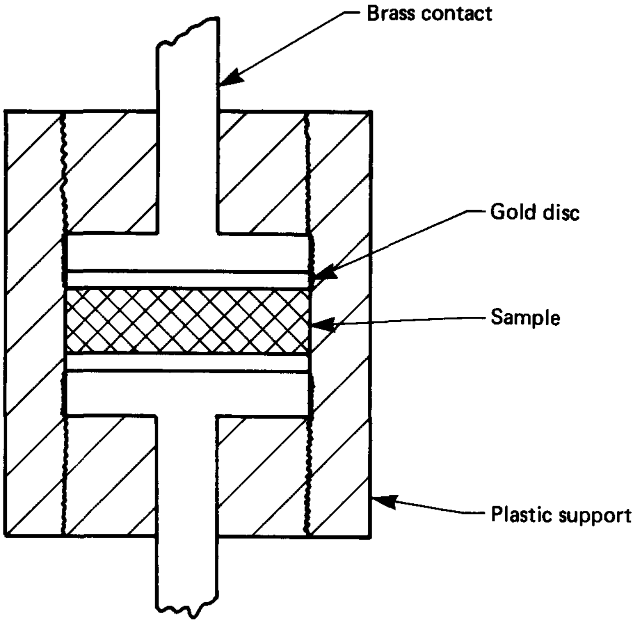


Figure 1 Cell used for conductivity measurements on pressed pellets

RESULTS AND DISCUSSION

In a previous investigation we have used some [Rh(L–L)chel]PF_6 complexes (L–L = cod; chel = bipy, 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline, 5,6-dimethyl-1,10-phenanthroline, 3,4,7,8-tetramethyl-1,10-phenanthroline) as catalysts for the polymerization of phenylacetylene (PA)[7]. In the presence of NaOH as co-catalyst, all these complexes are very active, giving linear polymers of the substrate.

Wehave now studied comparatively in reactions with BPA and PA the catalytic activity of a series of Rh complexes of the general formula [Rh(L–L)chel]X in which we have varied the diolefin, the nitrogen chelating ligand and the counterion. Here we will give the results of the reactions with BPA and the reactions of PA will be the subject to the next paper.

We have now examined also the catalytic activity of the platinum complex $[Pt(C{\equiv}C{-}CH_2NHCN_2Ph)_2(PPh_3)_2]$ because previously we have observed[8] that platinum acetylides are also active catalysts for the linear polymerization of acetylene derivatives.

The catalytic activity of the various complexes is given in *Table 1*. The complex [Rh(cod)(bipy)]X (X = PF_6), which was very active in reactions carried out with PA (50% of PPA in 5 min)[7], is less active in reactions with BPA, and only about 20% of polymer PBPA is obtained in 8 h, under similar experimental conditions.

The counterion influences the catalytic activity of the [Rh(cod)(bipy)]X complexes; the ClO_4 and BPh_4 anions give better yields of polymer than PF_6; the highest yield was obtained in the presence of [Rh(cod)(bipy)]ClO_4.

In order to examine the influence of the nitrogen chelating ligands we have prepared two complexes with chel = dipyam and bpz. Both these complexes were more active than the analogous complex of bipy. The best yield (about 70% of PBPA) was obtained in the presence of the complex [Rh(cod)(bpz)]PF_6.

We have also varied the unsaturated ligand of the complex and prepared two complexes of bipy and dipyam with nbd.

Table 1 Polymerization reactions of *N*-benzylpropargylamine (BPA) in the presence of Rh complexes

Catalyst	PBPA yield (%)	Molecular weight[a]		Ratio of units I_5^-/monomer	Conductivity (ohm^{-1} cm^{-1})
		A	B		
$[Rh(cod)(bipy)]PF_6$	17.7		2300	0	10^{-14}
				0.34	10^{-5}
				0.68	1
$[Rh(cod)(bipy)]ClO_4$	40.9	3400	1100	0	10^{-13} (A)
				0.17	10^{-10} (A)
				0.34	10^{-5} (A), 10^{-6} (B)
				0.68	4 (A), 2 (B)
$[Rh(cod)(bipy)]B(Ph)_4$	25.3	2800	1400	0	10^{-10} (A), 10^{-13} (B)
				0.17	10^{-6} (A), 10^{-9} (B)
				0.34	4 (A), 10^{-6} (B)
				0.68	2 (B)
$[Rh(cod)(dipyam)]PF_6$	41.3		1300	0	10^{-13}
				0.17	10^{-9}
				0.34	10^{-4}
				0.68	6
$[Rh(cod)(bpz)]PF_6$	68.2	3700	1500	0	10^{-12} (A), 10^{-13} (B)
				0.17	10^{-6} (A), 10^{-10} (B)
				0.34	10^{-4} (A), 10^{-5} (B)[b]
				0.68	3 (A), 7 (B)
$[Rh(nbd)(bipy)]PF_6$	10.2	1500			
$[Rh(nbd)(dipyam)]PF_6$	25.3		1400	0	10^{-13}
				0.34	10^{-6}
				0.68	5
$[Pt(C{\equiv}CCH_2NHCH_2Ph)_2(PPh_3)_2]$	10.2		1500	0	10^{-13}
				0.17	10^{-6}
				0.34	4

[a] Fraction A insoluble in CCl_4, fraction B soluble in CCl_4

[b] The same value was obtained by dissolving the pellet in THF and reprecipitating with petroleum ether

The catalytic activity was markedly lower for both derivatives. This result suggests that during the polymerization reaction the BPA coordinates to the rhodium atom in competition with the diolefin.

Under analogous conditions the platinum bisacetylide $[Pt(C{\equiv}CCH_2NHCH_2Ph)_2(PPh_3)_2]$ complex was less active than the rhodium compounds.

Polymers with molecular weight in the range 1000–2000 were obtained with all these catalysts for the PBPA fractions soluble in CCl_4. Higher molecular weight fractions are present in the residues insoluble in CCl_4, which were obtained in reactions carried out in the presence of $[Rh(cod)bipy]X$ ($X = ClO_4$, BPh_4), $[Rh(cod)bpz]PF_6$ and $[Rh(nbd)bipy]PF_6$ (*Table 1*).

The elemental analyses (C and H) of PBPA polymers are in good agreement with the theoretical values; therefore no spontaneous and rapid oxidation of PBPA occurs.

We have also determined the amount of Rh present in PBPA samples. We have found the presence of Rh (0.7–0.8%) in PBPA samples purified by dissolution in CCl_4 and precipitation with petroleum ether. The same amount of Rh was determined in some samples dissolved in water acidified with H_2SO_4 and reprecipitated with NaOH. These results seem to indicate that Rh atoms of the catalysts interact with the double bonds of the polymer chain better than with the nitrogen atoms of the pendant groups. In the latter case the Rh–N bonds should probably be cleaved by treatment with a strong acid like H_2SO_4 used to dissolve the polymer and lower Rh contents should be found in polymer samples purified by the acid–base treatment.

I.r. and n.m.r. spectra

The i.r. spectra of PBPA are given in *Figure 2*. The polymers obtained in the presence of the $[Rh(cod)(bipy)]X$ ($X = PF_6$, ClO_4, BPh_4) complexes show different i.r. spectra (*Figures 2a*, *2b*, *2b'* and *2c*). The difference is mainly due to the intensity variation of some bands. For instance, the band at 840 cm^{-1}, which is very intense in spectrum *2a*, is very weak in spectra *2b*, *2b'* and *2c*. Also the bands at 700–735, 760 and 790 cm^{-1} have different intensities in the four spectra.

Intensity variations of the bands in this spectral region have been associated with variations of the structure of polyenic systems. The band at 740 cm^{-1}, due to the out-of-plane deformation vibrations of the C–H bonds, is characteristic for a *cis* structure in polyacetylene[9]. Furthermore Simionescu[10] proposed a formula for the determination of the *cis* content of poly(phenylacetylene) based on the ratio between the intensity of two bands at 760 and 740 cm^{-1}.

Therefore it is probably also true for PBPA polymers that variations of intensity of the i.r. bands are due to different structures of polymeric chains.

The spectra (*2d* and *2e*) of the PBPA obtained in the presence of $[Rh(nbd)chel]PF_6$ complexes (chel = bipy, dipyam) exhibit bands of different intensity in the region 700–800 cm^{-1}, but in both spectra the band at 840 cm^{-1} is rather intense.

BPA in the presence of the $[Rh(cod)bpz]PF_6$ catalyst gives two polymer fractions. The fraction insoluble in CCl_4 shows an i.r. spectrum *2f* similar to that of the soluble polymer, obtained in the presence of the complex $[Rh(cod)dipyam]PF_6$ (*2g*). The other fraction of the

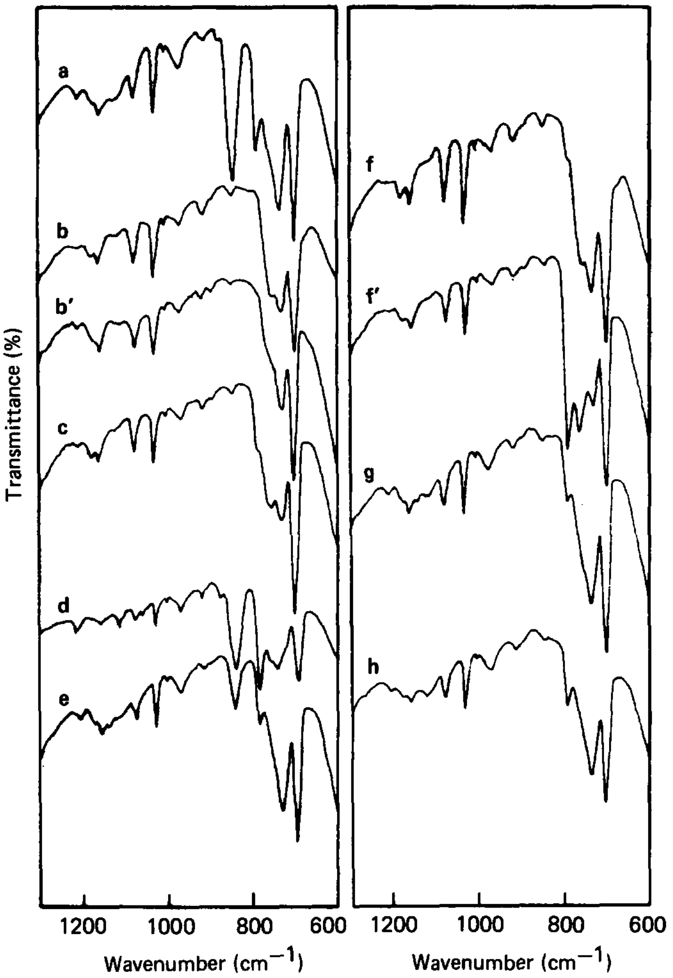


Figure 2 I.r. spectra (nujol mulls) of PBPA obtained with various catalysts: (a) [Rh(cod)(bipy)]PF_6; (b) [Rh(cod)(bipy)]ClO_4 (PBPA insoluble in CCl_4); (b') [Rh(cod)(bipy)]ClO_4; (c) [Rh(cod)(bipy)]$B(Ph)_4$; (d) [Rh(nbd)(bipy)]PF_6; (e) [Rh(nbd)(dipyam)]PF_6; (f) [Rh(cod)(bpz)]PF_6 (PBPA insoluble in CCl_4); (f') [Rh(cod)(bpz)]PF_6; (g) [Rh(cod)(dipyam)]PF_6; (h) $[Pt(C{\equiv}CCH_2NHCN_2Ph)_2(PPh_3)_2$

polymer obtained in the presence of [Rh(cod)bpz]PF_6 complex shows an i.r. spectrum *2f'* with a peculiar feature in the region 700–800 cm^{-1}, viz. a band at 790 cm^{-1} of unusual intensity.

The spectrum *2h* of the polymer obtained in the presence of the $[Pt(C{\equiv}C{-}CH_2NHCH_2Ph_5)_2(PPh_3)_2]$ complex is similar to spectra *2a*, *2e* and *2g* in the region 700–800 cm^{-1} but, like the spectrum *2g*, the 840 cm^{-1} band is of low intensity.

The i.r. spectra of two samples of doped PBPA are shown in *Figure 3*. Although obtained from polymers prepared with different catalysts and exhibiting different i.r. spectra in the undoped form (*Figures 2g* and *2g'*), these spectra are very similar.

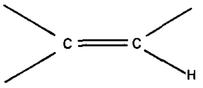
An isomerization from *cis* to *trans* structure induced by addition of I_2 as doping agent has been observed in the case of polyacetylene[11]. PBPA polymers probably behave analogously.

The ^1H n.m.r. spectra of PBPA polymers are shown in *Figure 4* where, by comparison, we have reported also the ^1H n.m.r. spectrum of BPA. This spectrum (*4a*) is characterized by a sharp signal at $\delta = 7.23$ ppm (against tetramethylsilane (TMS)) of the protons of the benzene ring; a signal at $\delta = 3.8$ ppm is due to the protons of the CH_2 group bonded to the phenyl ring. The doublet at 3.30 ppm is assigned to the protons of the CH_2 group which are coupled with the hydrogen of the $C{\equiv}C{-}H$ group. The triplet at 2.05 ppm is due to the hydrogen of the $C{\equiv}CH$ group and the singlet at 1.2 ppm to the NH group.

The ^1H n.m.r. spectra of fractions insoluble in CCl_4 (*Figures 4b*, *4c* and *4d*) exhibit broad signals at $\delta = 7.3$–7.2 ppm; and four signals at $\delta = 4.8$, 3.8, 2.9 and 2.3 ppm, which are sharp signals, over a wide resonance observed in the region 1–5 ppm.

The signal at 3.8 ppm is due to CH_2 groups as in the spectrum of the monomer. The other signals are shifted as a consequence of the formation of the polymeric chain.

The signal at 4.8 ppm can be due to the



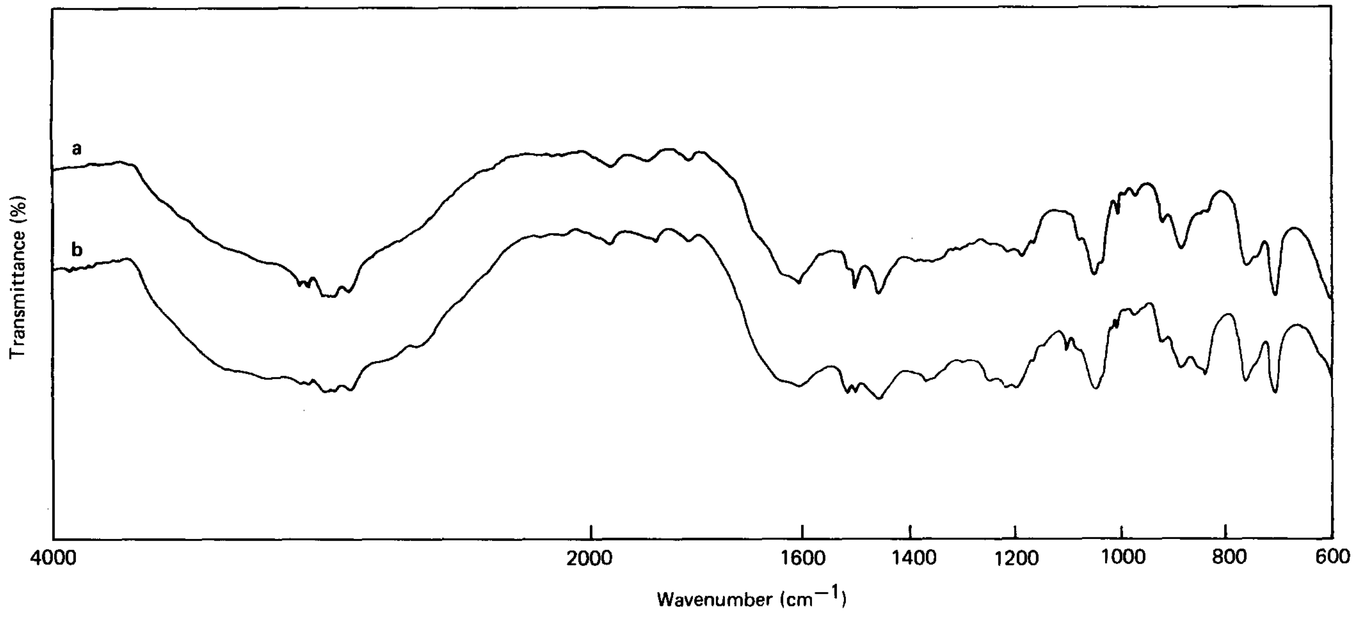


Figure 3 I.r. spectra of iodine-doped PBPA (I_5^-/monomer = 0.68) with two catalysts: (a) [Rh(cod)(bpz)]PF_6; (b) [Rh(cod)(dipyam)]PF_6

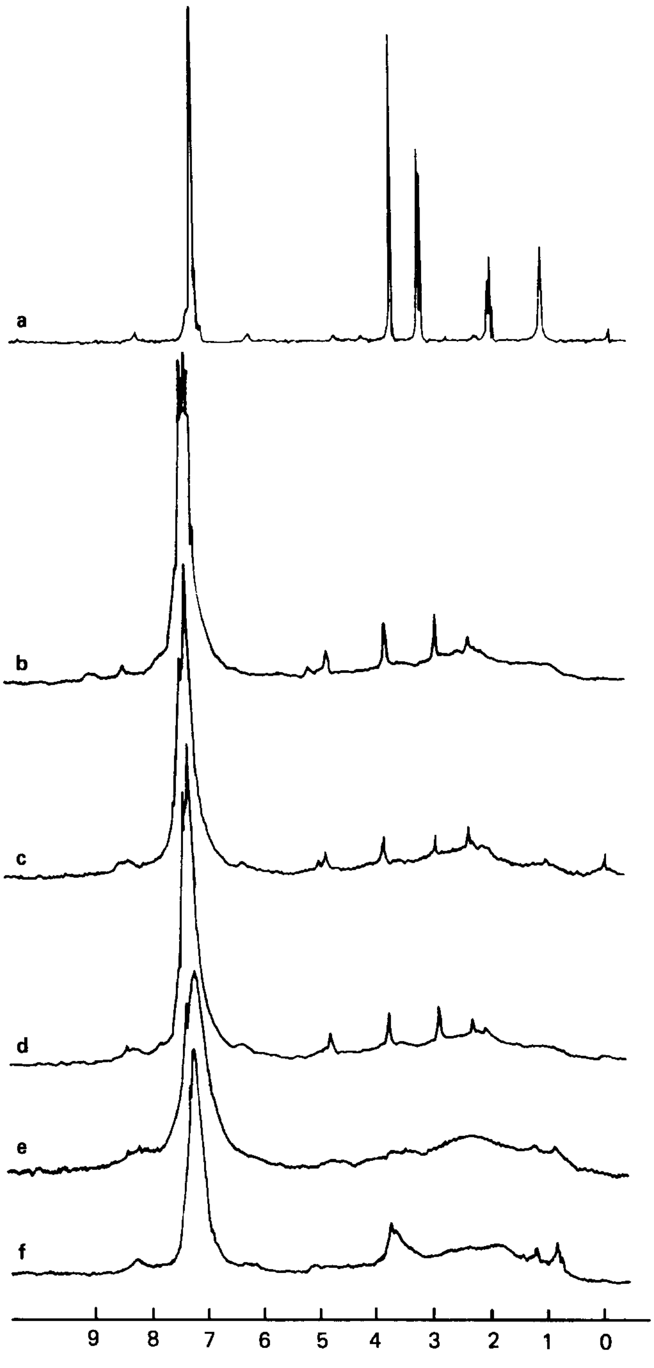


Figure 4 ^{1}H n.m.r. spectra of PBPA obtained with various catalysts: (a) *N*-benzylpropargylamine; (b) $[Rh(cod)(bipy)]B(Ph)_4$ (PBPA insoluble in CCl_4); (c) $[Rh(cod)(bpz)]PF_6$ (PBPA insoluble in CCl_4); (d) $[Rh(cod)(bipy)]ClO_4$ (PBPA insoluble in CCl_4); (e) $[Rh(cod)(bipy)]ClO_4$, $[Rh(cod)(bipy)]BPh_4$, $[Rh(cod)(bpz)]PF_6$, $[Rh(nbd)(bipy)]PF_6$; (f) $[Rh(cod)(bipy)]PF_6$, $[Rh(nbd)(dipyam)]PF_6$, $[Rh(cod)(dipyam)]PF_6$, $[Pt(C{\equiv}CCH_2NHCH_2CPh_2)_2(PPh_3)_2]$, Solvent: (b), (c), (d), $CDCl_3$; (e), (f), CCl_4

hydrogens. The multiplet at 7.3 ppm is attributed to the hydrogens of the benzene ring. The broadening of the 7.3 ppm resonance is probably caused by different chemical environments due to different orientations of the benzene rings in the polymer.

The ^{1}H n.m.r. spectra of the PBPA obtained by precipitation with petroleum ether of the fractions soluble in CCl_4 are shown in *Figures 4e* and *4f*. The spectrum *4e* is characteristic of the polymers obtained with the complexes $[Rh(cod)bipy]X$ ($X = ClO_4$, BPh_4), $[Rh(cod)bpz]PF_6$ and $[Rh(nbd)bipy]PF_6$; the spectrum *4f* is characteristic of the polymers obtained with the complexes $[Rh(cod)chel]PF_6$ (chel = bipy, dipyam), $[Rh(nbd)dipyam]PF_6$ and $[Pt(C{\equiv}CCH_2NHCH_2Ph)_2(PPh_3)_2]$. There is no clear correlation between the i.r. and ^{1}H n.m.r. spectra of PBPA polymers.

The spectra of *Figure 4* show a wide resonance between 1 and 5 ppm. A weak wide resonance between 2.0 and 4.5 ppm was observed by Simionescu in the ^{1}H n.m.r. spectra of poly(phenylacetylene). The broad resonance was assigned to the methinic protons of 1,3- and 1,4-cyclohexadiene structures formed during thermal isomerization of the chain from a *cis–transoidal* to a *trans–cisoidal* structure[12]. Perhaps analogous cyclohexadiene structures are present in PBPA polymers obtained with Rh(I) catalysts.

Conductivity measurements

Undoped pellets of PBPA have conductivities of about 10^{-13}–10^{-12} ohm^{-1} cm^{-1}. By doping the polymers with increasing amounts of I_2 we have found a continuous increase of conductivity (*Table 1*).

In a preceding investigation on polymers of phenylacetylene (PPA) the analysis of far infra-red and Raman spectra revealed the presence of I_5^- as predominant species in PPA samples doped with various amounts of I_2[13]. Assuming that I_5^- units are formed also in the PBPA polymers, we have increased the amount of doping agent to 0.68 units of I_5^- (75% I_2 by weight) for each monomer unit in the polymer. At this high dopant concentration gummy materials are obtained, as reported before, which exhibit high conductivity (10–100 ohm^{-1} cm^{-1}). These gummy materials are stable for long periods if they are stored in closed vessels. Exposed to air they become slowly solid, losing solvent and in part iodine. The conductivity decreases to 10^{-5} ohm^{-1} cm^{-1}.

The undoped PBPA is also stable in air: a pellet of PBPA used for a conductivity measurement was powdered and the i.r. and n.m.r. spectra of the powder were found to be identical to those of the starting material; a new measurement of conductivity was in good agreement with the previous one.

When doping was carried out by the two procedures in the experimental section, similar conductivity values were measured at the same dopant concentrations, thus proving the good stability of such systems.

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